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Short communication

The investigation of resin degradation in catalyst layer of proton exchange membrane fuel cell

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HIGHLIGHTS

- A simple method is provided to isolate the membrane degradation in situ.
- The resin degradation of catalyst layer is specially discussed.
- The prominent degradation location at open circuit operation is discussed.

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ABSTRACT

In order to separate resin degradation in catalyst layer (CL) from membrane degradation of proton exchange membrane fuel cell (PEMFC), Fluorine emission rate (FER) was specially selected to highlight the degradation of Nafion® resin in CL by employing hydrocarbon membrane as membrane. The drain water from the cathode and anode was collected and analyzed separately. It is found that FERs of drain water are 0.065 μmol cm^{-2} h^{-1} (cathode) and 0.049 μmol cm^{-2} h^{-1} (anode), suggesting resin degradation happened in CLs and the predominant degradation occurred in the cathode in open circuit operation.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have received much attention and great interest in the past decades, due to the possibility of converting the chemical energy directly into the electrical energy electrochemically with high efficiency and low emission of pollutants [1,2]. It is commonly believed that chemical degradation of the proton exchange membrane (PEM) proceeds. To date, considerable effort has been devoted to the mechanism of PEM degradation [3]. However, the chemical degradation of Nafion® resin in catalyst layer has not drawn particular attention.

As we know, the Pt/C catalyst, carbon paper, PTFE suspension and Nafion® solution (DuPont) are used in the MEA preparation. The Nafion® loading in both the anode and the cathode is commonly 0.4 mg cm^{-2} or more [4]. The Nafion® loading is little, but it contributes much to the performance of PEMFCs. Therefore, the investigation of Nafion® resin degradation in catalyst layer is imperative for appropriate experimental design.

This study is aimed at illuminating the behavior of Nafion® resin in catalyst layer (CL) during open circuit voltage (OCV) test. In order to isolate the chemical degradation from PEM degradation, hydrocarbon membrane like sulfonated poly (ether ether ketone) (SPEEK) is specially selected to replace Nafion® membrane. Due to no fluorine in SPEEK membrane, fluorine emission rate (FER) of the drain water of anode or cathode side is able to be an indicator of resin degradation in CL.

2. Experimental

2.1. Preparation of membrane and membrane electrode assembly (MEA)

Sulfonated poly(ether ether ketone) (SPEEK) polymers were prepared following the procedure reported in the literature [5,6].

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The ion exchange capacity (IEC) of SPEEK, which is determined by titration, is 1.41 mmol g^{-1}.

Two homemade electrodes with effective area 5 cm^2 were hot-pressed onto a membrane to form a MEA at 140 °C and 1 MPa for 1 min. The resulting MEA was placed in a single cell, which employs stainless steel as the end plates and stainless steel mesh as the current collectors. The Pt loadings of the anode and cathode electrodes were 0.3 mg cm^{-2} and 0.7 mg cm^{-2}, respectively. The dry Nafion® loading of the anode and cathode were 0.4 mg cm^{-2} and 0.6 mg cm^{-2} [4].

2.2. Fourier transform infrared spectroscopy (FT-IR) spectrum analysis

FT-IR spectra of membranes were conducted by using a JASCO FT-IR 4100 spectrometer. Each spectrum, which was recorded as the average of 48 scans with a resolution of 4 cm^{-1}, was collected from 1800 to 580 cm^{-1} in reflection mode [7,8].

2.3. In situ open circuit voltage (OCV) test

The MEAs were subjected to in-situ OCV test at 80 °C, 0.2 MPa and 50% RH. H_2/O_2 were fed to the anode/cathode of the cell, respectively. The gas flow rate was 40 ml min^{-1}. The test was run for 24 h for each MEA, and the drain water from the cathode and anode was condensed in cold-traps separately. The open circuit voltages were recorded once per hour. Plain sample (recast Nafion® membrane) is from the previous work [9].

2.4. Fluorine emission rate (FER)

An ion chromatography system (ICS-90, DIONEX) was employed to detect the concentration of fluoride ions in the sample [10]. Prior to analysis, hydrogen peroxide must be completely decomposed to obtain accurate and reproducible results [11].

2.5. Linear sweep voltammetry (LSV) measurement

CHI 600B electrochemical workstation was employed to record the limiting oxidation current of the crossover hydrogen, in order to evaluate the gas permeability of the membrane before and after the OCV test. H_2 gas (40 ml min^{-1}) and N_2 gas (100 ml min^{-1}) were fed to the anode and the cathode, respectively. By applying a dynamic potential to the cathode from 0 V to 0.6 V versus the anode with the scan rate of 5 mV s^{-1} at 0.2 MPa, 80 °C and 100% RH, the H_2 oxidation current was measured [12].

3. Results and discussions

3.1. Characterization of SPEEK membrane

As shown in Fig. 1, the absorption peaks at 1252, 1080, 1021 and 709 cm^{-1} are assigned to the sulfonic acid group of SPEEK, and the absorption at 1646 cm^{-1} is ascribed to the carbonyl band of SPEEK [6]. The result indicates that SPEEK membrane was obtained by the sulfonation of poly(ether ether ketone) (PEEK) resin.

3.2. Resin degradation characterization

Open circuit voltage (OCV) test is usually employed to accelerate the chemical degradation of membrane [13]. F^- emission rate (FER) is usually recorded to quantify the extent of membrane degradation. Generally all eyes are on membrane degradation. This work is aimed to throw some light on the resin degradation in catalyst layer. However, the procedures are the same with the way to

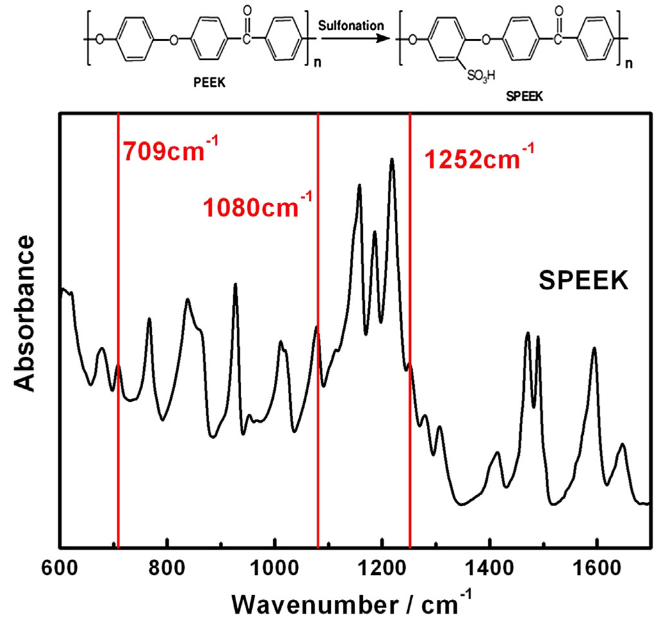

Fig. 1. The reflective FT-IR spectrum of SPEEK membrane.

quantify membrane degradation. The drain water of each side is condensed in cold-traps separately and detected by ion chromatography system to obtain the concentration of F^-. The difference is that SPEEK is a hydrocarbon membrane without fluorine. SPEEK membrane plays three important roles here: 1) providing in situ operation condition; 2) isolating resin degradation in catalyst layer from membrane degradation; 3) separating the anode degradation from the cathode degradation. Two interesting conclusions may be drawn: 1) if F^- can be detected in the drain water from SPEEK based MEA, the resin degradation in catalyst layer is detected; 2) the prominent degradation location at open circuit operation can be confirmed due to the comparison of FER of both sides.

The analyses are almost the same with those of membrane degradation. As shown in Fig. 2, the SPEEK membrane shows a more stable OCV. The OCV decay rate of SPEEK is 0.6 mV h^{-1}, which is about a tenth part of that of recast Nafion® membrane. The differences are attributed to a lower gas permeability of SPEEK [14],

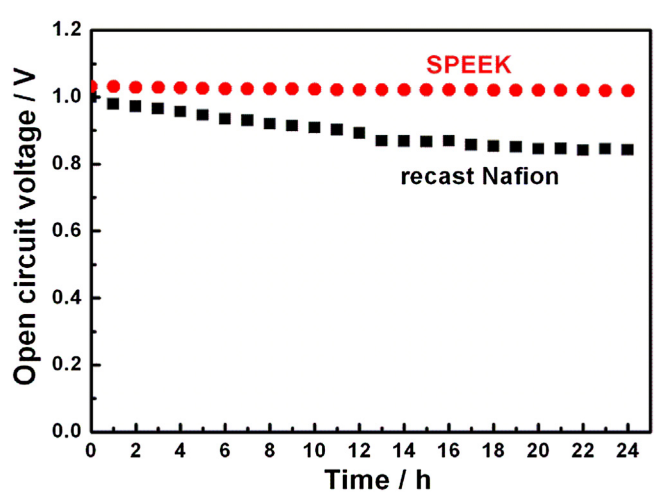

Fig. 2. Durability comparison of SPEEK and recast Nafion® membranes during OCV tests (cell temperature: 80 °C; saturator temperature: 64 °C; RH: 50%; anode gas: H_2; cathode gas: O_2; flow rate: 40 ml min^{-1} at anode and cathode; and duration: 24 h).

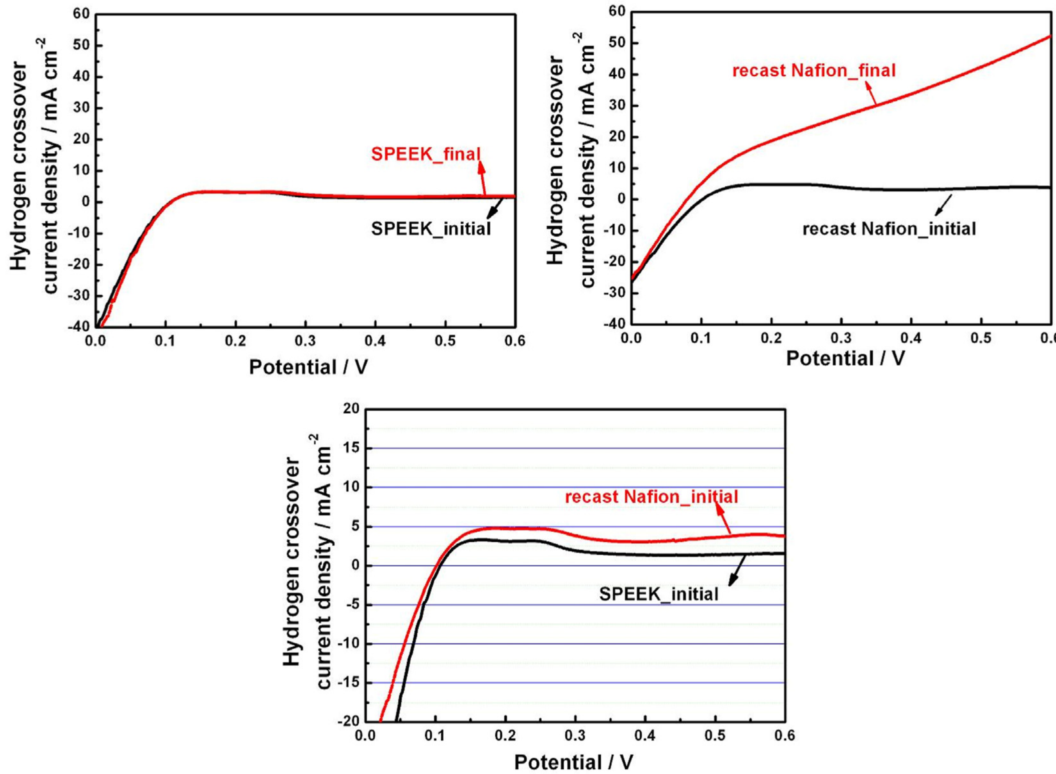

Fig. 3. Hydrogen crossover current density for H_2/N_2 cell with different membranes before and after the OCV tests (cell temperature: 80 °C; saturator temperature: 80 °C; RH: 100%; anode gas: H_2; cathode gas: N_2; flow rate: 40 ml min^{-1} at anode and 100 ml min^{-1} at cathode, respectively).

which is confirmed by linear sweep voltammetry (LSV) measurement. As Fig. 3 shows, the initial limiting current density of SPEEK at 400 mV is only 44% of that of recast Nafion® membrane, indicating the initial gas permeability of SPEEK is only 44% of that of recast Nafion® membrane. Less crossover gas will result in less free radicals, which could be caused by the chemical combination of crossover gas and gas on the catalyst [15]. After 24 h OCV test, the hydrogen crossover current density of recast Nafion® membrane increases a lot, by contrast, that of SPEEK membrane does not change. As we know, the disadvantage of hydrocarbon membrane is its poor oxidative stability. It is found SPEEK membrane shows good performance at open circuit operation when compared to Nafion® membrane with excellent chemical stability [16].

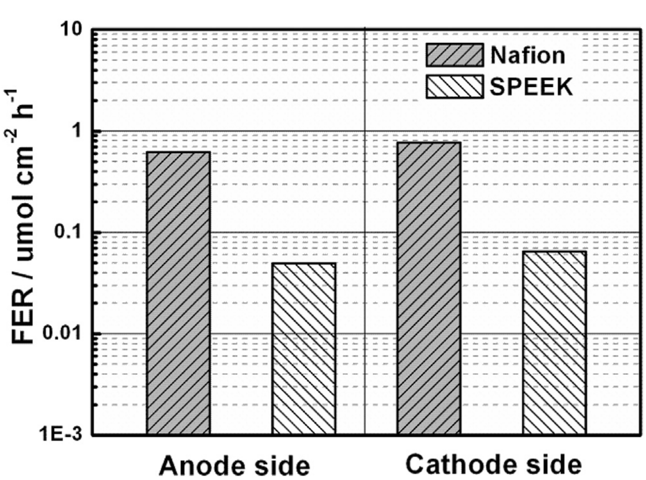

Fig. 4. FERs (μmol cm^{-2} h^{-1}) measured for recast Nafion® and SPEEK based MEAs during OCV test.

As shown in Fig. 4, FER of recast Nafion® membrane is much more than that of SPEEK membrane. It's consistent with the results of OCV test (Fig. 2) and LSV test (Fig. 3). More importantly, FER of SPEEK membrane is not equal to zero, suggesting the Nafion® resin in the catalyst layer undergoes the chemical degradation because of no fluorine in SPEEK membrane. Cathode FER of recast Nafion® is great than its anode FER, indicating that the prominent degradation occurs in cathode side at open circuit operation. Moreover, cathode FER of SPEEK membrane is bigger than its anode FER. Due to no fluorine in SPEEK membrane, degradation at anode is absolutely isolated from the one at cathode. Therefore, it is further confirmed that the prominent degradation happens to the cathode side at open circuit operation.

4. Conclusions

In order to isolate the membrane degradation from the degradation of Nafion® resin in the catalyst layer, SPEEK membrane is subjected to open circuit voltage test and fluorine emission rate is specially picked out to illustrate the degradation. It is found that the degradation of Nafion® resin occurs at both sides at open circuit operation and the prominent degradation happens at cathode sides. SPEEK membrane shows good performance at open circuit voltage test when compared to Nafion® membrane with excellent chemical stability.

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